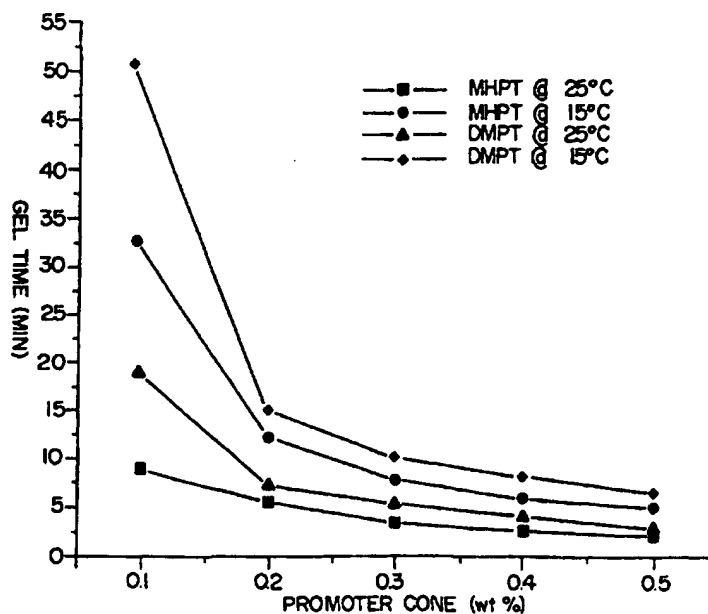




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>C08K 5/18, C08L 67/06</b>		A1	(11) International Publication Number: <b>WO 97/35916</b>
			(43) International Publication Date: 2 October 1997 (02.10.97)
(21) International Application Number: PCT/US97/04589		(74) Agents: SUMMA, Philip et al.; Bell, Seltzer, Park & Gibson, P.O. Drawer 34009, Charlotte, NC 28234 (US).	
(22) International Filing Date: 21 March 1997 (21.03.97)			
(30) Priority Data: 08/624,980 28 March 1996 (28.03.96) US		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(60) Parent Application or Grant (63) Related by Continuation US 08/624,980 (CON) Filed on 28 March 1996 (28.03.96)			
(71) Applicant (for all designated States except US): FIRST CHEM- ICAL CORPORATION [US/US]; 1001 Industrial Road, Pascagoula, MS 39581-3237 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): SANTOBIANCO, John, Gabriel [US/US]; East Belle Fontaine Beach Road, Ocean Springs, MS 39564 (US). GEIGER, Cary, Cecil [US/US]; 2513 San Jacinto, Gautier, MS 39553 (US). BOWERS, Joseph, Stanton, Jr. [US/US]; 65 South Georgia Avenue, Mobile, AL 36604 (US).		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: METHODS OF CURING UNSATURATED POLYMERS USING TERTIARY AROMATIC AMINE CURE PROMOTERS



## (57) Abstract

Methods of promoting the cure of unsaturated polymer resins with a peroxide initiator by including as a promotor N-alkyl-N-(2-hydroxyalkyl)-p-toluidines. The use of the tertiary aromatic amines as a promotor provides a fast cure at a wide range of temperatures. Polymerizable compositions and methods of applying the same to a surface are also described.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

-1-

**METHODS OF CURING UNSATURATED POLYMERS  
USING TERTIARY AROMATIC AMINE CURE PROMOTERS**

Field of the Invention

The present invention relates to methods for curing unsaturated polymer resins, and more particularly to curing such resins with a peroxide  
5 initiator in the presence of a cure promoter.

Background of the Invention

The term polyester refers generally to the group of synthetic resins that are polycondensation products of dicarboxylic acids with dihydroxy alcohols.  
10 The term unsaturated polyester resin, as used herein, designates a linear-type alkyd possessing carbon-to-carbon double bond unsaturation in the polymer chain. These unsaturated polyesters may be crosslinked and thus cured by reaction with monomers such as styrene or  
15 diallyl-phthalate, usually in the presence of a peroxide to form insoluble and infusible resins without the formation of a by-product during the curing reaction. Other types of polymer resins are also known which include carbon-to-carbon double bond unsaturation  
20 in the polymer chain, and which can also be crosslinked and cured, such as urethane acrylates, epoxy acrylates, and the like.

Because of their versatility and cost effectiveness, these resins possess broad commercial  
25 utility. Such utilities include, but are not limited to, low-pressure laminating; attractive and durable coatings for concrete, masonry, wood, plastic, wallboard, and metal; specialty resins targeted for synthetic marble, boat hulls, polymer concrete, mine-  
30 bolt resins, transfer molding, restorative dentistry, automotive body repair, and the like.

-2-

Tertiary aromatic amines are widely used as cure promoters or accelerators for unsaturated resins in the presence of peroxide initiators. Exemplary tertiary amines useful as cure promoters include, for example, N,N-dimethylaniline (DMA), N,N-diethylaniline (DEA), N-(2-hydroxyethyl)-N-methyl aniline, N-(2-hydroxyethyl)-N-ethyl aniline, N,N-bis-(2-hydroxyethyl)-m-toluidine, N-(2-hydroxyethyl)-N-[2-(2-hydroxyethoxy) ethylaniline, N,N-bis-(2-hydroxyethyl)-p-toluidine (HEPT), and N,N-dimethyl-p-toluidine (DMPT). However, cure rates for these types of compounds could be improved.

Further, as such uses demonstrate, polyester resins and other crosslinkable resins are often used in environments, i.e., outdoors, where temperatures cannot be easily controlled. Accordingly, it has become increasingly important to increase the cure rate of such polymer resins at low temperatures without detracting from the physical properties of the resins. The effectiveness of tertiary amine cure promoters such as those listed above, however, can fall off dramatically at low temperatures. Further, while the N,N-dimethyltoluidines are known as effective cure promoters at temperatures as low as 10°C to 15°C, these compounds become much less effective at temperatures approaching or below 0°C.

In addition, the lower dialkylanilines and toluidines can be toxic and can produce irritating and offensive odors; can be corrosive; and cannot sufficiently cure the polymer surface.

#### Objects and Summary of the Invention

It is accordingly an object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which will provide a fast cure

-3-

without adversely affecting the physical properties of the resins.

It is another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which will provide a fast cure at low temperatures.

It is another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which is essentially odorless.

It is yet another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which is less toxic than lower dialkylanilines and toluidines.

It is yet another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which is substantially non-corrosive.

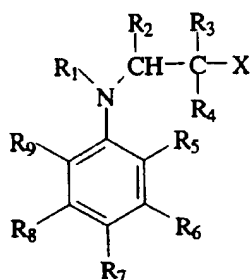
It is yet another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which can provide a more complete surface cure.

It is yet another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which can be incorporated into the polymer backbone.

It is yet another object of the present invention to provide a method for curing unsaturated polymer resins in the presence of a peroxide initiator using a cure promoter which is relatively inexpensive and thus cost effective.

-4-

These and other objects of the present invention will become apparent from the following general and detailed description of the invention. The objects of the present invention are accomplished based on the discovery that compounds according to Formula (I) below can be very effective cure promoters. In the invention, an unsaturated polymer is cured with a peroxide initiator in the presence of a promoter according to Formula I:



10 (I)  
wherein:

$\text{R}_1$  is linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl;

$\text{R}_2$  is H, linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl, wherein said C1 to C6 alkyl or C3 to C6 cycloalkyl is optionally substituted at the C1 or C3 position, respectively, by X as defined below;

$\text{R}_3$  and  $\text{R}_4$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, and C3 to C6 cycloalkyl;

$\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$ , and  $\text{R}_9$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, C3 to C6 cycloalkyl, and C1 to C6 alkoxy; and

25  $\text{X}$  is OH,  $\text{OR}_1$ , CN,  $\text{OC(O)R}_1$ ,  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{H}$  or  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{R}_1$ , wherein  $m = 1$  to 6 and  $n = 1$  to 6, and wherein  $\text{R}_1$  is as defined above.

-5-

Currently preferred are compounds of Formula (I) wherein:

$R_1$  is methyl or ethyl;

$R_2$  is H or hydroxymethyl;

5  $R_3$  or  $R_4$  are each independently selected from the group consisting of H, methyl and ethyl;

$R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ , and  $R_9$  are each independently selected from the group consisting of H and methyl; and

10  $X$  is OH or  $O[(CH_2)_mO]_nH$ , wherein  $m = 2$  and  $n = 1$  to 6.

Exemplary compounds of Formula I in accordance with the invention include, but are not limited to, N-methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT); N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT);  
15 and N-methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT).

In the invention, the promoter is present in an amount sufficient to increase the cure rate of the unsaturated resin to about 75%, preferably about 60%, and more preferably about 50%, of the cure time of the  
20 unsaturated resin measured using N,N-dimethyl-p-toluidine. The cure promoter can be present, for example, in an amount between about 0.01 and about 5 percent by weight based on the weight of unsaturated resin, and preferably in an amount between about 0.1  
25 and about 0.5 percent by weight. The cure promoters are particularly effective for use with unsaturated polyester resins as known in the art, but are also useful as cure promoters for other unsaturated polymer  
30 acrylates, and the like.

The use of the cure promoters of Formula I provides a substantial increase in gel and cure rates of polymerizable unsaturated polymers, as compared to conventional tertiary amine cure promoters, such as  
35 DMA, DMPT, and the like. Further, the use of these cure promoters provides advantages in terms of gel and cure rates at a wide range of temperatures. The cure

-6-

promoters can be very effective cure promoters at ambient temperatures, i.e., about 20-25°C, and can also be effective at low temperatures, i.e., as low as 15°C, 0°C and lower. Promoters of Formula I gradually lose effectiveness at decreasing temperatures. In contrast, various other tertiary amines, such as DMA, DEA, HEPT and DMPT, dramatically lose their effectiveness as a cure promotor at decreasing temperatures, i.e., particularly temperatures at or below 0°C.

10           The present invention also provides polymerizable compositions characterized by accelerated polymerization, which include a polymerizable unsaturated polymer resin; a peroxide initiator; and a cure promotor according to Formula I; as well as  
15           methods for bonding a polymerizable composition to a surface of a substrate.

#### Brief Description of the Drawings

Some of the features and advantages of the invention having been stated, others will become  
20           apparent from the detailed description which follows, and the accompanying drawings which form a part of the original disclosure of this invention, and in which:

Figure 1 is a graph illustrating gel time in minutes for an unsaturated polyester resin versus  
25           promotor concentration in weight percentage using 1% benzoyl peroxide at 15°C and 25°C;

Figure 2 is a graph illustrating cure time in minutes for an unsaturated polyester resin versus  
promotor concentration in weight percentage using 1%  
30           benzoyl peroxide at 15°C and at 25°C;

Figure 3 is a graph illustrating gel time in minutes for an unsaturated polyester resin versus  
promotor concentration in weight percentage using 1%  
benzoyl peroxide at 0°C and at 25°C; and

35           Figure 4 is a graph illustrating cure time in minutes for an unsaturated polyester resin versus



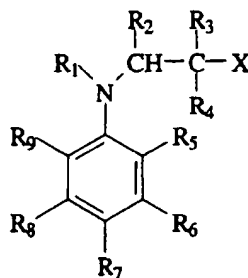
- 7 -

promotor concentration in weight percentage using 1% benzoyl peroxide at 0°C and at 25°C.

### Detailed Description of the Invention

The present invention will now be described more fully hereinafter with reference to the accompanying drawings, in which illustrative embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiment set forth in here. Rather, this embodiment is provided so that the disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

The cure promoters of the invention are compounds according to Formula (I) below:



(I)

wherein:

R<sub>1</sub> is linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl;

R<sub>2</sub> is H, linear or branched C1 to C6 alkyl, or C3 to C6 cycloalkyl, wherein said C1 to C6 alkyl or C3 to C6 cycloalkyl is optionally substituted at the C1 or C3 position, respectively, by X as defined below;

R<sub>3</sub> and R<sub>4</sub> are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, and C3 to C6 cycloalkyl;

-8-

$R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ , and  $R_9$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, C3 to C6 cycloalkyl, and C1 to C6 alkoxy; and

- 5                   X is OH,  $OR_1$ , CN,  $OC(O)R_1$ ,  $O[(CH_2)_mO]_nH$  or  $O[(CH_2)_mO]_nR_1$ , wherein  $m = 1$  to  $6$  and  $n = 1$  to  $6$ , and wherein  $R_1$  is as defined above.

Currently preferred are compounds of Formula (I) wherein:

- 10                    $R_1$  is methyl or ethyl;  
                     $R_2$  is H or hydroxymethyl;  
                     $R_3$  or  $R_4$  are each independently selected from the group consisting of H, methyl and ethyl;  
                     $R_5$ ,  $R_6$ ,  $R_7$ ,  $R_8$ , and  $R_9$  are each independently  
15 selected from the group consisting of H and methyl; and  
                    X is OH or  $O[(CH_2)_mO]_nH$ , wherein  $m = 2$  and  $n = 1$  to  $6$ .

As used herein, the term "C1 to C6 alkyl" refers to C1 to C6 linear or branched alkyl, such as  
20 methyl, ethyl, propyl, butyl, isopropyl, sec-butyl, and tert-butyl, butyl, pentyl, isopentyl, and hexyl. The term "cycloalkyl" as used herein refers to C3 to C6 cyclic alkyl, such as cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl. The term "alkoxy" as used  
25 herein refers to C1 to C6 linear or branched oxygen-substituted alkyl, such as methoxy, ethoxy, propyloxy, butyloxy, isopropyloxy, and t-butyloxy.

Exemplary compounds of Formula I in accordance with the invention include, but are not  
30 limited to, N-methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT); N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT); and N-methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT).

In accordance with the present invention, the compounds of Formula I have been found to provide a  
35 substantial increase in gel and cure rates of polymerizable unsaturated resins in the presence of a peroxide initiator, as compared to conventional

-9-

tertiary amine cure promoters, such as DMA, DMPT, and the like. Further, the use of these cure promoters provides advantages in terms of gel and cure rates at a wide range of temperatures. That is, the cure  
5 promoters in accordance with the present invention can be very effective at ambient temperatures, i.e., about 20-25°C. However, the use of the cure promoters of Formula I is also very advantageous at low temperatures, i.e., as low as 15°C, 0°C and lower.

10 This result is unexpected and surprising because various other tertiary amines, such as DMA, DEA, HEPT and DMPT, dramatically lose their effectiveness as cure promoters at decreasing temperatures, i.e., particularly temperatures at or  
15 below 0°C. That the cure promoters of Formula I also provide increased gel and cure rates at a wide range of temperatures is also unexpected and surprising based upon the structure of the amines of the invention. For  
20 example, the structure of the promoters of the invention (for example MHPT) would lead one skilled in the art to expect the reactivity of the cure promoters of the invention to fall between that of N,N-dialkyl-p-toluidines (for example DMPT) and N,N-dihydroxyalkyl-p-toluidines (for example HEPT). Instead, the reactivity  
25 of MHPT is much greater than DMPT, which is in turn greater than HEPT.

The compounds of Formula I used in accordance with the method of the invention can be used in quantities between about 0.01 and about 5 percent by  
30 weight, preferably in quantities between about 0.1 and about 1 percent by weight, and more preferably between about 0.1 and 0.5 percent by weight, based on weight of the unsaturated resin.

The compounds used in accordance with the  
35 invention can be used individually. However, mixtures thereof can also be used.

-10-

The compounds of the invention can be prepared using techniques as known in the art, for example, alkylation of an appropriate N-alkyl-p-toluidine to provide, for example, an N-alkyl-N-(2-hydroxyalkyl)-p-toluidine. For example, MHPT can be prepared by adding a slight molar excess of ethylene oxide to N-methyl-p-toluidine and subjecting the mixture to conditions sufficient to ethoxylate the toluidine compound. The ethoxylation can be performed by methods known in the art.

The compounds of the present invention can also be synthesized by alkylation of an appropriate N-hydroxyalkyl-p-toluidine. For example, MHPT can be prepared by adding formaldehyde and hydrogen to a mixture of N-hydroxyethyl-p-toluidine and palladium on a carbon catalyst under appropriate temperature and pressure conditions, such as at 120°C and 120 psig.

The material obtained by the first route is usable directly out of the reactor. No further purification is required, but distillation can be performed to provide a purer product. The material from the second route should be purified before use.

Polyesters which are useful according to the present invention include conventional unsaturated polyester resins known in the art. Thus, the unsaturated polyesters may be obtained by reaction of approximately equivalent amounts of a polyvalent alcohol such as ethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, propylene glycol, pentaerythritol, and other diols or polyols with an unsaturated dibasic carboxylic acid or carboxylic anhydride such as maleic acid, maleic anhydride, fumaric acid, itaconic acid, or citraconic acid. These unsaturated dibasic carboxylic acids or anhydrides are often used in combination with aromatic and/or saturated aliphatic dicarboxylic acids or the anhydrides derived therefrom, such as phthalic acid,

-11-

phthalic anhydride, isophthalic acid, tetrachlorophthalic acid, malonic acid, adipic acid, sebacic acid, tartaric acid, and the like.

Unsaturated polyesters containing vinyl groups or vinylidene groups may be obtained by polycondensation of alpha,beta-unsaturated monocarboxylic acids such as acrylic or methacrylic acid, with mono-, di- or polyhydric alcohols. Exemplary alcohols include methanol, ethanol, isopropanol, cyclohexanol, phenol, ethylene glycol, propylene glycol, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxycyclohexyl)propane, 2,2-bis(4-beta-hydroxyethyloxy-phenyl)propane, pentaerythritol and dimers thereof, trimethol propane and a glycerol, and the complex diols or polyols. Unsaturated polyesters containing vinyl groups or vinylidene groups also may be obtained by reacting alpha,beta-unsaturated monocarboxylic acids with compounds containing epoxy groups, such as bisphenol A bis(glycidyl ether).

Further, the unsaturated polyesters can be dissolved in monomers copolymerizable with the polyester, which contain one or more C=C groups such as styrene, vinyl toluene, methylmethacrylate, ethyleneglycolmethacrylate, and the like, as is also conventional. The preferred solutions are those which contain from about 70 to 50 percent by weight of unsaturated polyester and 30 to 50 percent by weight of copolymerizable monomer. Styrene is a preferred copolymerizable monomer.

Although the invention has been described in detail with regard to the use of the compounds according to Formula (I) as cure promoters for unsaturated polyester resins, the skilled artisan will appreciate that the compounds of the invention can also be used with other unsaturated polymers capable of being cured using peroxide initiators. Such unsaturated polymers include conventional polyurethane

-12-

acrylate resins known in the art. The unsaturated polyurethane may be obtained by reaction of a polyisocyanate, such as toluene diisocyanate, diphenylmethane diisocyanate, hexamethylene diisocyanate, and the like, with an appropriate compound containing at least two active hydrogen atoms, such as a polyol or a polyamine. Exemplary polyols include ethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, propylene glycol, pentaerythritol, and other diols or polyols. Urethane polymers may be used in the form of homopolymers or, more preferably, with various other monomers which can be copolymerized therewith. For example, urethane polymers can be prepared by reacting any of a variety of acrylic comonomers, such as acrylic and methacrylic acids, and their amides, esters, salts and corresponding nitriles, with the polyurethane resin. Particularly suitable comonomers for such polymers are methyl methacrylate, ethyl acrylate and acrylonitrile.

Yet another exemplary unsaturated polymer which can be treated using the compounds of Formula (I) include unsaturated epoxy resins known in the art. Unsaturated epoxy resins may be obtained by reaction of an epoxide group (resulting from the union of an oxygen atom with two other atoms, usually carbon), such as epichlorohydrin, oxidized polyolefins, for example ethylene oxide, with an aliphatic or aromatic alcohol such as bisphenol A, glycerol, etc. As with the unsaturated polymers described above, the epoxy resins may be used in the form of homopolymers or copolymers with various other comonomers which can be reacted therewith, including various acrylic monomers, such as acrylic and methacrylic acids, and their amides, esters, salts and corresponding nitriles.

To improve the stability of the unsaturated polyesters, inhibitors are commonly used in amounts ranging from about 0.001 to 0.03 percent by weight.

-13-

The most commonly used inhibitors are hydroquinone, hydroquinone monomethyl ether, quinone, and p-tert-butyl catechol. To more accurately control the comparison tests above, no inhibitor was used in the comparative examples.

The polymerization or copolymerization initiators which can be used are those conventionally available and include hydrogen peroxide, the ketone peroxides, such as acetylacetone peroxide, methylethylketone peroxide, cyclohexanone peroxide and methylisobutylketone peroxide; the diacyl peroxides, such as benzoyl peroxide, lauroyl peroxide, isobutyryl peroxide, acetyl peroxide, 2,4-dichlorobenzoyl peroxide, succinic acid peroxide, decanoyl peroxide, diisononanoyl peroxide; the peresters, such as tert-butyl peroxide-2-ethyl hexanoate; the perketals, such as 1,1-ditert-butylperoxy-3,3,5-trimethyl cyclohexane and dialkyl peroxides, such as 1,3-bis(tert-butylperoxyisopropyl) benzene. The diacyl peroxides, and particularly benzoyl peroxide, are the preferred initiators. The initiators are used in amounts known in the art, for example, for peroxide initiators, between about 0.5 and 10 percent by weight.

The present invention will be further illustrated by the following non-limiting examples.

EXAMPLE 1  
Synthesis of  
N-methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT)

N-(2-hydroxyethyl)-p-toluidine, 50 g, was combined with 1 g 5% palladium on carbon catalyst and charged to a pressure reactor. The pressure reactor was heated to 120°C and fed hydrogen gas to maintain 120 psig pressure. Formaldehyde, 178 g 37% solution in water, was fed to the pressure reactor over 10 hours. After hydrogen uptake ceased, the reaction mass was filtered to remove catalyst and decanted to separate the aqueous phase.

-14-

The organic phase was charged to a vacuum distillation apparatus. Water and low boilers were removed. N-methyl-N-(2-hydroxyethyl)-p-toluidine product was collected at overhead temperatures around 148°C. Melting point was 28-30°C.

EXAMPLE 2  
Synthesis of  
N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT)

N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT) was prepared substantially as described above in Example 1, except that acetaldehyde was added to ethylate N-(2-hydroxyethyl)-p-toluidine.

EXAMPLE 3  
Synthesis of  
N-methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT)

N-methyl-p-toluidine, 29.3 g, and methanol, 50 g, were placed in a reactor. Propylene oxide, 25.4 g, was slowly added to the reactor over two hours. Afterwards, the reactor was heated under reflux for 6 hours. The low boilers were removed by distillation. Then, the mixture was vacuum distilled to give 2HPMT. The boiling point is 92°C at 5 mm Hg.

EXAMPLE 4  
Comparison of Gel and Cure Times of  
MHPT and DMPT at 15°C and 25°C

The thus synthesized MHPT was compared to N,N-dimethyl-p-toluidine (DMPT) as described below with regard to gel and curing rates of an unsaturated polyester resin at varying promoter concentrations levels and varying temperatures. Benzoyl peroxide was used as a 50% dispersion in tricresyl phosphate and which was used as the initiator for the curing reaction. The polyester resin used was an unpromoted, high-reactivity resin based on ortho phthalic acid and containing 20 to 25 percent free styrene monomer,



-15-

available under the trade name PolyLite 44-289 from Reichhold Chemical Company.

MHPT was compared to DMPT as cure reaction promoters at five different concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 percent by weight) for the unsaturated polyester resin. All the curing reactions were performed using 1% benzoyl peroxide as initiator at two different reaction temperatures (15°C and 25°C). The balance of the composition was the polyester resin.

The base formulation used in this experimental was as follows:

Benzoyl peroxide dispersion (50%)	2.00 g
Tertiary aromatic amine	0.1 to 0.5 g
Polyester resin	<u>Balance</u>
Total mass	= 100 g

All curing reactions were performed at either 15°C or 25°C using a wide-mouth ½ pint mason jar suspended in a constant temperature water bath. A reacting mass of 100 grams was used in all cases. The procedure utilized was as follows: The amine promotor was weighed into a clean-dry jar to an accuracy of  $\pm 0.001$  gram using a ground glass syringe for transfer. The proper quantity of resin was then weighed into the jar. The jar was placed into the constant temperature water bath and allowed to equilibrate for 30 minutes.

Next,  $2 \pm 0.0075$  grams benzoyl peroxide dispersion was weighed onto the end of a wooden tongue blade. A lab timer was activated, and the benzoyl dispersion was mixed thoroughly into the resin by stirring for three minutes with the blade, gently to avoid air entrapment. The reacting mass was probed periodically with the blade, and the gel time was recorded as the time from introduction of the initiator

-16-

to the point when the resin snapped back from the blade in a rubbery manner.

Next, a thermometer wrapped in aluminum foil was inserted into the center of the gelled resin. The  
5 cure time was recorded as the time from addition of the initiator to peak exotherm, i.e., the maximum temperature reached.

The effect of promotor concentration on the gel and cure times at these two reaction temperatures  
10 is depicted in Figures 1 and 2. Figure 1 illustrates that at a promotor level of 0.1%, gel time for MHPT is only about 60% to 70% of the time measured for DMPT. Figure 2 illustrates that at a promotor level of 0.1%,  
15 cure time for MHPT is only about 53% to 60% of the time measured for DMPT. Further, MHPT yielded faster gel and cure times than did DMPT at each tested level of promotor concentration and at each tested temperature.

#### EXAMPLE 5

##### *Comparison of Gel and Cure Times of 20 MHPT and DMPT at 0°C and 25°C*

MHPT was also compared to DMPT as a cure reaction promotor using the procedure described above in Example 4, except for the following changes. MHPT was compared to DMPT at five different concentrations  
25 (0.4, 0.5, 0.6, 0.7 and 0.8 percent by weight) for the unsaturated polyester resin. Again, all the curing reactions were performed using 1% benzoyl peroxide as initiator at the two different reaction temperatures (in this example 0°C and 25°C). The balance of the  
30 composition was the polyester resin, PolyLite 44-289.

The effect of promotor concentration on the gel and cure times at these two reaction temperatures is depicted in Figures 3 and 4. Figures 3 and 4 show that MHPT yielded faster gel and cure times than did  
35 DMPT at each tested level of promotor concentration and at each tested temperature. Figure 3 illustrates that at a promotor level of 0.4% and 0°C, gel time for MHPT

-17-

is only about 65% of the time measured for DMPT. Figure 4 illustrates that at a promotor level of 0.4% and at 0°C, cure time for MHPT is only about 70% of the time measured for DMPT. Thus, MHPT is particularly  
5 advantageous as a cure reaction promoter as compared to DMPT at temperatures approaching 0°C.

## EXAMPLE 6

Comparison of Gel and Cure Times of  
MHPT, EHPT and 2HPMT with

10 Various Tertiary Amines at Ambient Temperature

Gel and cure rates of various N-alkyl-(2-hydroxyalkyl)-p-toluidine promoters of the invention (EHPT, 2HPMT, and MHPT) were evaluated as described above in Examples 4 and 5, except the polyester resin  
15 used was an unpromoted, low-reactivity resin based on orthophthalic acid and containing 32 to 36 percent free styrene monomer, available under the trade name Polylite 44-285 from Reichhold Chemical Company. Gel and cure rates were evaluated at two different promoter  
20 concentrations (0.2 and 0.3 percent by weight). All reactions were performed using 1% benzol peroxide as an initiator at ambient (i.e., 20-25°C). The balance of the composition was polyester.

The effect of promotor concentration on the  
25 gel and cure times is set forth in Table 1 below. DMA is N,N-dimethyl-aniline; MHA is N-methyl-N-hydroxyethyl-aniline; 3HPMT is N-methyl-(3-hydroxypropyl)-p-toluidine; BDA is N,N-dimethyl-tert-butyl aniline; and DMPT is N,N-dimethyl-p-toluidine.

-18-

Table 1

Amine	.2% by Weight		.3% by Weight	
	Gel Seconds	Cure Minutes	Gel Seconds	Cure Minutes
DMA	1980	56	1275	35
MHA	1765	45	1140	32
3HPMT	555	26	330	17
BDA	560	24	405	18.5
DMPT	420	19	265	14.5
EHPT	356	17	265	13.3
2HPMT	300	16.5	217.5	11.5
MHPT	295	16	245	11.8

5

10

As illustrated in Table 1, the compounds in accordance with the invention yielded faster gel and cure times than did the other amines at each tested level of promotor concentration at ambient temperature. For example, at promoter concentrations of about 0.2 % by weight, the compounds of the invention exhibited cure rates of only about 20% of the time measured for DMA. At this same promoter concentration, the compounds of the invention exhibited cure rates of only about 70-75% of the time measured for DMPT, and only about 64-68% of the time measured for 3HPMT (an N-alkyl-N-(3-hydroxypropyl)-p-toluidine).

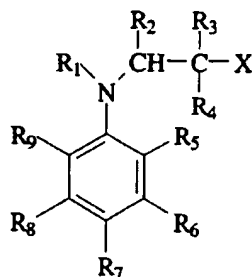
The foregoing examples are illustrative of the present invention and are not to be construed as limiting thereof. The invention is defined by the following claims, with equivalents of the claims to be included therein.

25

-19-

## THAT WHICH IS CLAIMED IS:

1. A method for curing unsaturated polymer resins, comprising curing an unsaturated polymer resin with a peroxide initiator in the presence of a promoter according to Formula I



5 (I)  
wherein:

$\text{R}_1$  is linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl;

10  $\text{R}_2$  is H, linear or branched C1 to C6 alkyl, or C3 to C6 cycloalkyl, wherein said C1 to C6 alkyl or C3 to C6 cycloalkyl is optionally substituted at the C1 or C3 position, respectively, by X as defined below;

15  $\text{R}_3$  and  $\text{R}_4$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, and C3 to C6 cycloalkyl;

$\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$ , and  $\text{R}_9$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, C3 to C6 cycloalkyl, and C1 to C6 alkoxy; and

20 X is OH,  $\text{OR}_1$ , CN,  $\text{OC(O)R}_1$ ,  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{H}$  or  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{R}_1$ , wherein  $m = 1$  to 6 and  $n = 1$  to 6, and wherein  $\text{R}_1$  is as defined above.

-20-

2. The method of Claim 1 wherein:

X is OH or  $O[(CH_2)_mO]_nH$ , wherein  $m = 1$  to 6  
and  $n = 1$  to 6.

3. The method of Claim 2 wherein:

5

$R_1$  is methyl or ethyl;

$R_2$  is H or hydroxymethyl;

$R_3$  and  $R_4$  are each independently selected from  
the group consisting of H, methyl and ethyl; and

X is OH or  $O[(CH_2)_mO]_nH$ , wherein  $m = 2$  and  $n =$   
10 1 to 6.

4. The method of Claim 1, wherein said  
promoter is selected from the group consisting of N-  
methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT); N-ethyl-  
N-(2-hydroxyethyl)-p-toluidine (EHPT); and N-methyl-N-  
15 (2-hydroxypropyl)-p-toluidine (2HPMT).

5. The method of Claim 1, wherein said  
promoter is present in an amount sufficient to increase  
the cure rate of said unsaturated resin to about 75% of  
the cure time of said unsaturated resin measured using  
20 N,N-dimethyl-p-toluidine.

6. The method of Claim 5, wherein said  
promoter is present in an amount sufficient to increase  
the cure rate of said unsaturated resin to about 60% of  
the cure time of said unsaturated resin measured using  
25 N,N-dimethyl-p-toluidine.

7. The method of Claim 6, wherein said  
promoter is present in an amount sufficient to increase  
the cure rate of said unsaturated resin to about 50% of  
the cure time of said unsaturated resin measured using  
30 N,N-dimethyl-p-toluidine.

-21-

8. The method of Claim 1, wherein said curing is at ambient temperature.

9. The method of Claim 1, wherein said curing is at a temperature about or below 15°C.

5 10. The method of Claim 1, wherein said curing is at a temperature about or below 0°C.

11. The method of Claim 1, wherein said promoter is present in an amount between about 0.01 and about 5 percent by weight based on the weight of  
10 unsaturated resin.

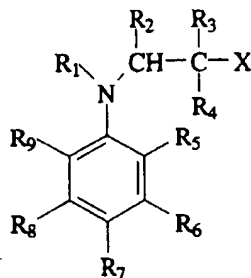
12. The method of Claim 11, wherein said promoter is present in an amount between about 0.1 and about 0.5 percent by weight based on the weight of unsaturated resin.

15 13. The method of Claim 1 wherein said unsaturated resin is selected from the group consisting of polyester, polyurethane, and epoxy resins.

14. The method of Claim 13 wherein said unsaturated resin is a polyester resin.

20 15. A method for curing unsaturated polyester resins, comprising curing an unsaturated polyester resin with a peroxide initiator in the presence of a promoter according to Formula I

- 22 -



(I)

wherein:

R<sub>1</sub> is methyl or ethyl;

R<sub>2</sub> is H or hydroxymethyl;

5 R<sub>3</sub> and R<sub>4</sub> are each independently selected from the group consisting of H, methyl and ethyl;

R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are each independently selected from the group consisting of H and methyl; and

10 X is OH or O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>H, wherein m = 1 to 6 and n = 1 to 6.

16. The method of Claim 15, wherein said promoter is present in an amount sufficient to increase the cure rate of said unsaturated polyester resin to about 75% of the cure time of said unsaturated polyester resin measured using N,N-dimethyl-p-toluidine.

17. The method of Claim 16, wherein said curing is at a temperature of about or below 0°C.

18. The method of Claim 16, wherein said curing is at ambient temperature.

19. A method for curing unsaturated polyester resins, comprising curing an unsaturated polyester resin with a peroxide initiator in the presence of a promoter selected from the group



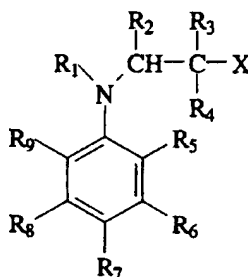
-23-

consisting of N-methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT); N-ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT); and N-methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT).

20. The method of Claim 19, wherein said curing is at a temperature of about or below 0°C.

21. The method of Claim 19, wherein said curing is at ambient temperature.

22. A polymerizable composition characterized by accelerated polymerization, comprising a polymerizable unsaturated polymer resin; a peroxide initiator; and a cure promoter according to Formula I



(I)

wherein:

15  $\text{R}_1$  is linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl;

$\text{R}_2$  is H, linear or branched C1 to C6 alkyl, or C3 to C6 cycloalkyl, wherein said C1 to C6 alkyl or C3 to C6 cycloalkyl is optionally substituted at the C1 or C3 position, respectively, by X as defined below;

20  $\text{R}_3$  and  $\text{R}_4$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, and C3 to C6 cycloalkyl;

$\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$ , and  $\text{R}_9$  are each independently selected from the group consisting of H, linear or

-24-

branched C1 to C6 alkyl, C3 to C6 cycloalkyl, and C1 to C6 alkoxy; and

X is OH, OR<sub>1</sub>, CN, OC(O)R<sub>1</sub>, O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>H or O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>R<sub>1</sub>, wherein m = 1 to 6 and n = 1 to 6, and  
5 wherein R<sub>1</sub> is as defined above.

23. The composition of Claim 22 wherein:

X is OH or O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>H, wherein m = 1 to 6  
and n = 1 to 6.

24. The composition of Claim 23 wherein:

10 R<sub>1</sub> is methyl or ethyl;  
R<sub>2</sub> is H or hydroxymethyl;  
R<sub>3</sub> and R<sub>4</sub> are each independently selected from  
the group consisting of H, methyl and ethyl; and  
X is OH or O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>H, wherein m = 2 and n =  
15 1 to 6.

25. The composition of Claim 22, wherein  
said promoter is selected from the group consisting of  
N-methyl-N-(2-hydroxyethyl)-p-toluidine (MHPT); N-  
ethyl-N-(2-hydroxyethyl)-p-toluidine (EHPT); and N-  
20 methyl-N-(2-hydroxypropyl)-p-toluidine (2HPMT).

26. The composition of Claim 22, wherein  
said promoter is present in an amount sufficient to  
increase the cure rate of said unsaturated resin to  
about 75% of the cure time of said unsaturated resin  
25 measured using N,N-dimethyl-p-toluidine.

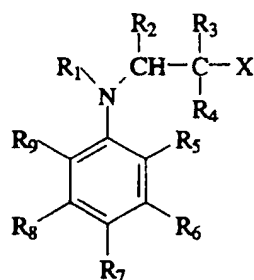
27. The composition of Claim 26, wherein  
said promoter is present in an amount sufficient to  
increase the cure rate of said unsaturated resin to  
about 60% of the cure time of said unsaturated resin  
30 measured using N,N-dimethyl-p-toluidine.

-25-

28. The composition of Claim 27, wherein said promoter is present in an amount sufficient to increase the cure rate of said unsaturated resin to about 50% of the cure time of said unsaturated resin  
5 measured using N,N-dimethyl-p-toluidine.

29. The composition of Claim 22 wherein said unsaturated resin is a polyester resin.

30. A method for curing unsaturated polyester resins, comprising curing an unsaturated  
10 polyester resin with a peroxide initiator in the presence of a promoter according to Formula I



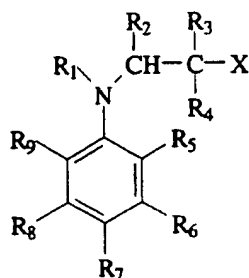
(I)

wherein:

- 15           R<sub>1</sub> is methyl or ethyl;  
              R<sub>2</sub> is H or hydroxymethyl;  
              R<sub>3</sub> and R<sub>4</sub> are each independently selected from  
 the group consisting of H, methyl and ethyl;  
              R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> are each independently  
 selected from the group consisting of H and methyl; and  
 20           X is OH or O[(CH<sub>2</sub>)<sub>m</sub>O]<sub>n</sub>H, wherein m = 1 to 6  
 and n = 1 to 6,  
              said promoter present in said composition in  
 an amount sufficient to increase the cure rate of said  
 unsaturated polyester resin to about 75% of the cure  
 25 time of said unsaturated polyester resin measured using  
 N,N-dimethyl-p-toluidine.

-26-

31. A method for bonding a polymerizable composition to a surface of a substrate, comprising:  
 applying to a surface of a substrate a polymerizable composition characterized by accelerated  
 5 polymerization, comprising a polymerizable unsaturated polymer resin; a peroxide initiator; and a cure promoter according to Formula I



(I)

wherein:

- 10  $\text{R}_1$  is linear or branched C1 to C6 alkyl or C3 to C6 cycloalkyl;  
 $\text{R}_2$  is H, linear or branched C1 to C6 alkyl, or C3 to C6 cycloalkyl, wherein said C1 to C6 alkyl or C3 to C6 cycloalkyl is optionally substituted at the C1 or  
 15 C3 position, respectively, by X as defined below;  
 $\text{R}_3$  and  $\text{R}_4$  are each independently selected from the group consisting of H, linear or branched C1 to C6 alkyl, and C3 to C6 cycloalkyl;  
 $\text{R}_5$ ,  $\text{R}_6$ ,  $\text{R}_7$ ,  $\text{R}_8$ , and  $\text{R}_9$  are each independently  
 20 selected from the group consisting of H, linear or branched C1 to C6 alkyl, C3 to C6 cycloalkyl, and C1 to C6 alkoxy; and  
 $\text{X}$  is OH,  $\text{OR}_1$ , CN,  $\text{OC(O)R}_1$ ,  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{H}$  or  $\text{O}[(\text{CH}_2)_m\text{O}]_n\text{R}_1$ , wherein  $m = 1$  to 6 and  $n = 1$  to 6, and  
 25 wherein  $\text{R}_1$  is as defined above; and  
 subjecting the surface having the polymerizable composition applied thereto to conditions sufficient to cure the composition.

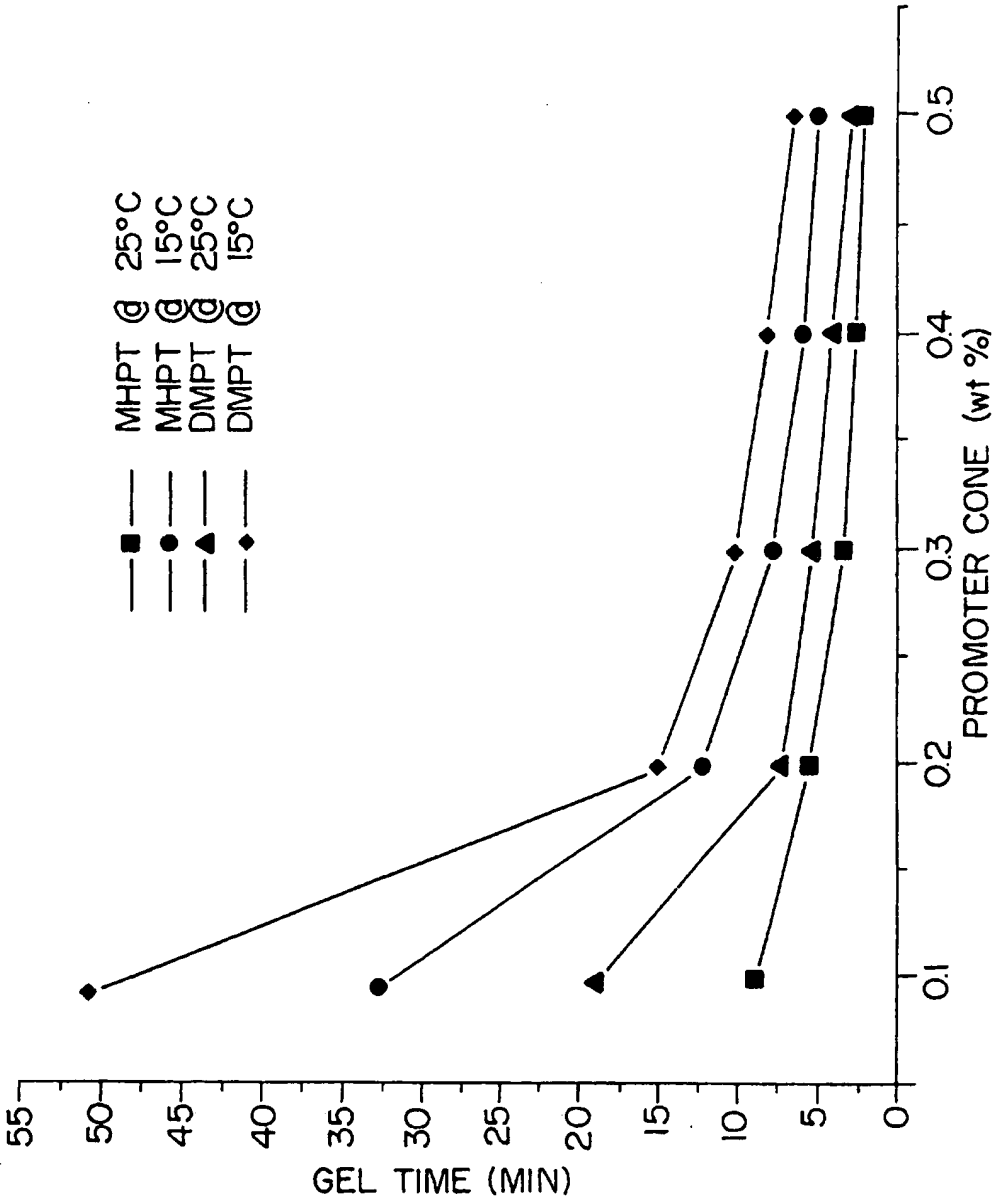
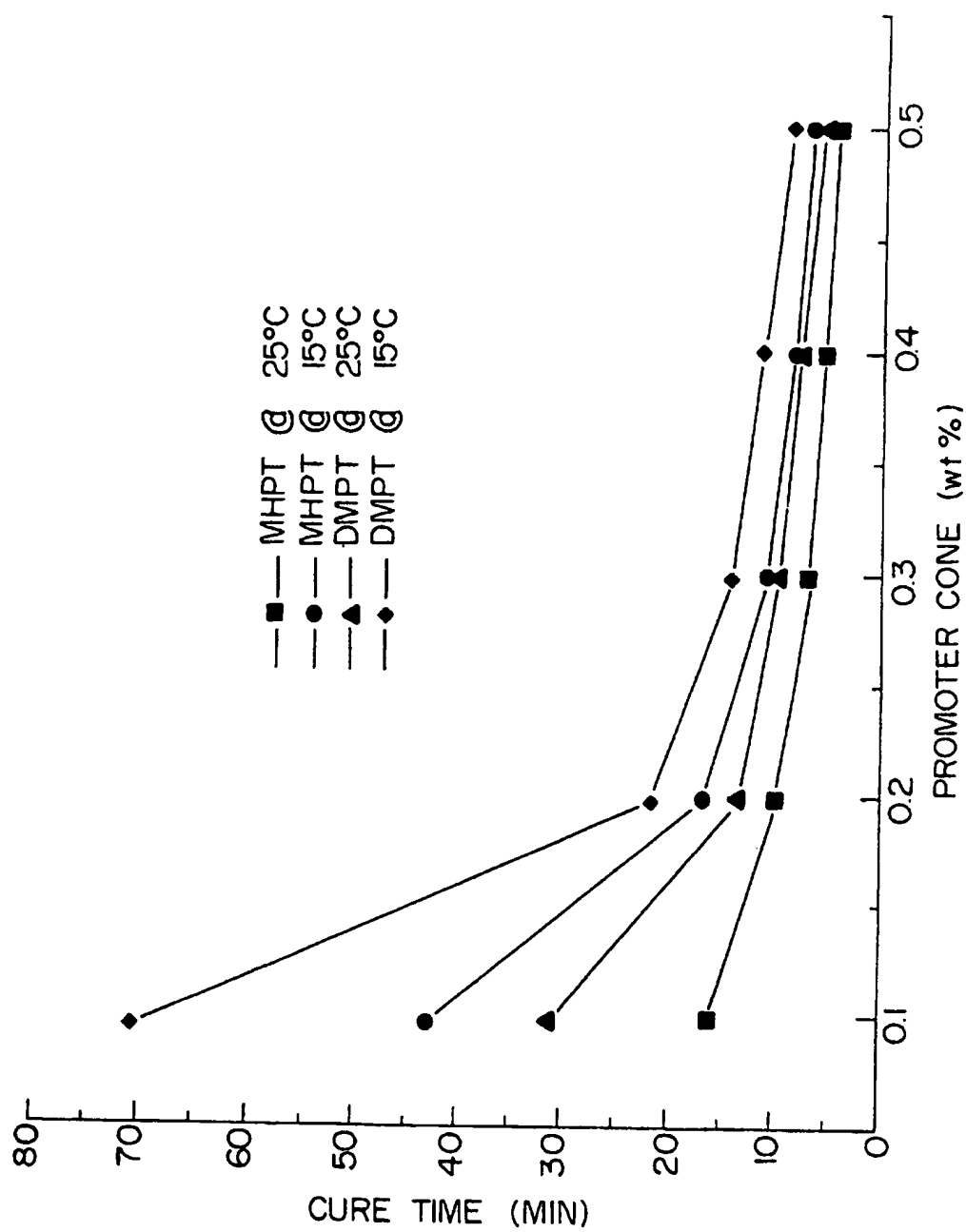


FIG. 1.

2/4

FIG. 2.

3/4

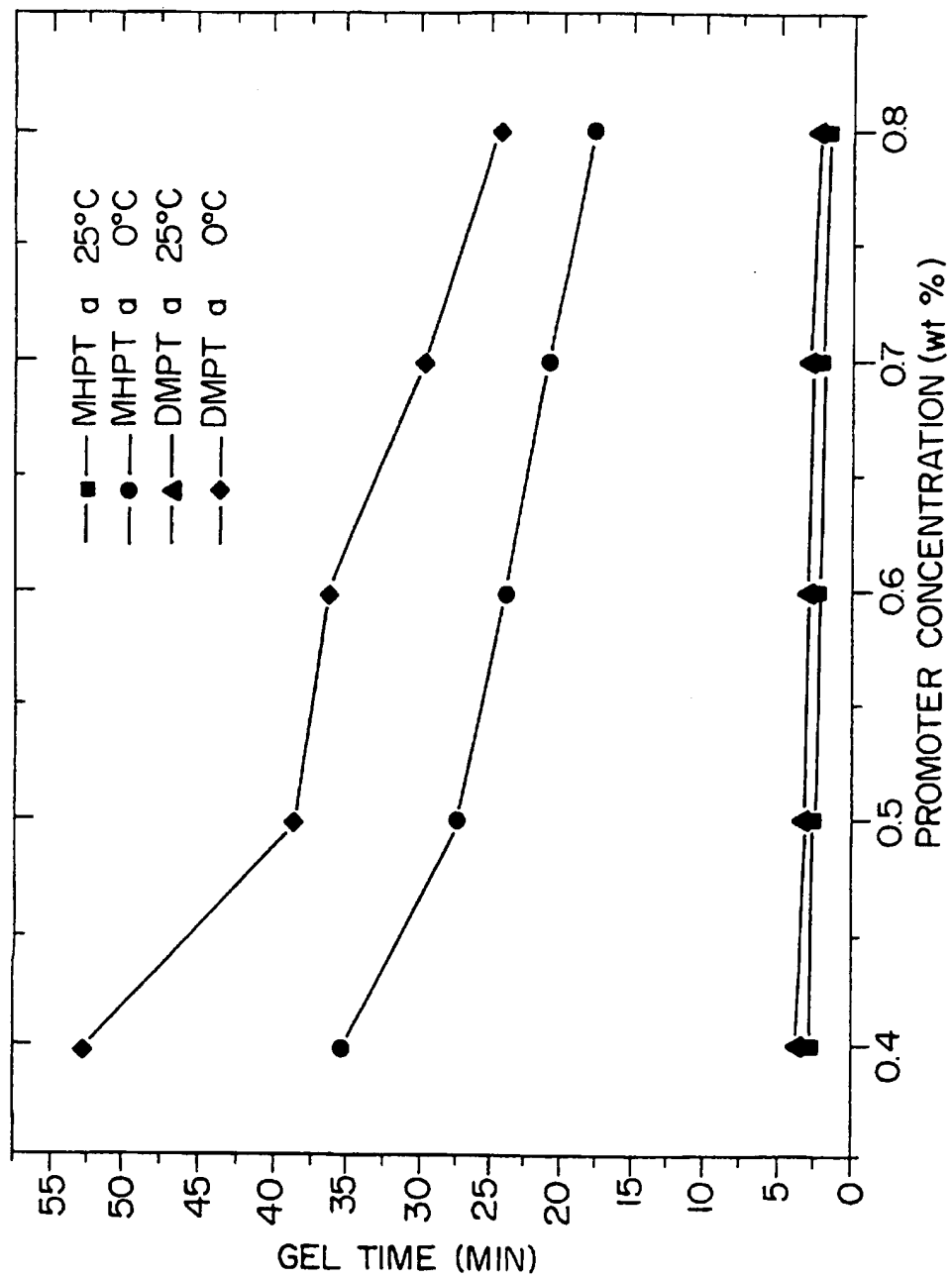
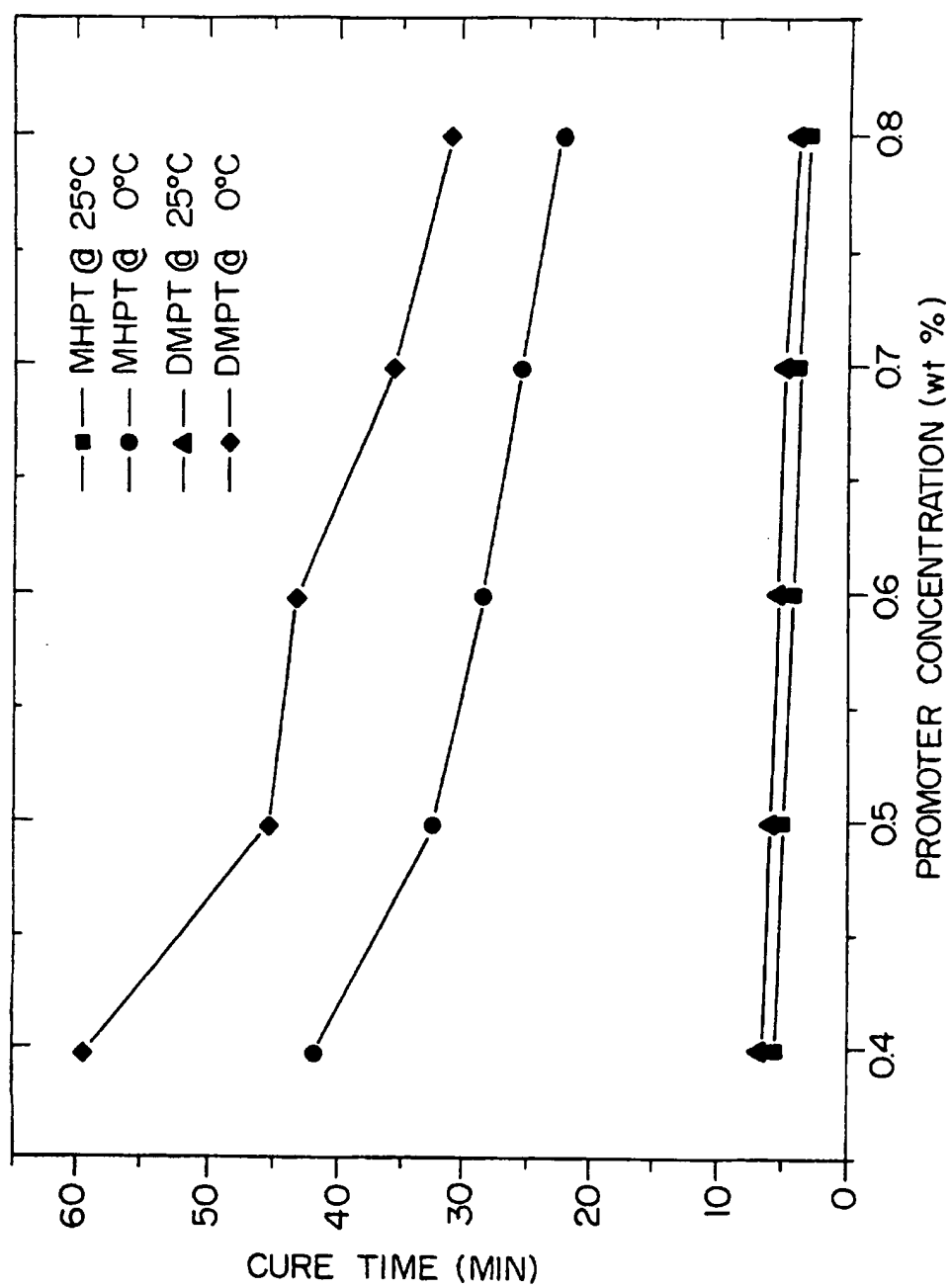


FIG. 3.

4/4

FIG. 4.



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/04589

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08K5/18 C08L67/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 074 564 A (BAYER) 23 March 1983	1,4,8, 13-16, 18,19, 21-25, 29-31
X	see page 6, line 15 see claims 1,6	1
X	GB 1 476 368 A (VIANOVA) 10 June 1977 see page 1, line 41 - page 2, line 5; examples; tables 1,2	1
A	US 3 950 287 A (COATS ET AL.) 13 April 1976	1,4, 13-15
X	see column 4, line 32 - line 45 see claims 1,5,10; examples	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

17 July 1997

Date of mailing of the international search report

21.08.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Engel, S

# INTERNATIONAL SEARCH REPORT

Internat. Application No  
PCT/US 97/04589

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 012 542 A (OSWITCH ET AL.) 15 March 1977	1-15
X	see column 4, line 30 - column 5, line 9 ---	1
A	CHEMICAL ABSTRACTS, vol. 81, no. 20, 18 November 1974 Columbus, Ohio, US; abstract no. 121658, DEMMLER ET AL.: "cold curing of ---" XP002035515 see abstract & KUNSTSTOFFE, vol. 64, no. 2, 1974, pages 78-86, ---	1-15
A	CHEMICAL ABSTRACTS, vol. 71, no. 16, 20 October 1969 Columbus, Ohio, US; abstract no. 71466, WERTS ET AL.: "cure promoters for --- unsaturated polyesters" XP002035516 see abstract & U.S. PAT. OFF., OFFIC. GAZ., vol. 864, no. 3, 1969, page 731 "us 790857 I" ---	1-15
A	GB 1 540 228 A (SCOTT BADER CO.) 7 February 1979 see column 1; claims 1-7 -----	1-15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/04589

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 74564 A	23-03-83	DE 3136292 A JP 58057415 A US 4421879 A	24-03-83 05-04-83 20-12-83
GB 1476368 A	10-06-77	AT 324004 A DE 2438675 A FR 2240933 A	11-08-75 06-03-75 14-03-75
US 3950287 A	13-04-76	NONE	
US 4012542 A	15-03-77	US 3914200 A	21-10-75
GB 1540228 A	07-02-79	AU 505579 B AU 2008276 A ZA 7606929 A	22-11-79 08-06-78 26-10-77